SUPPORING INFORMATION

Electrochemical Tuning of the Dielectric Function of Au Nanoparticles

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SUPPORTING INFORMATION

Raw Spectra

Below we provide spectra of the particles in the electrochemical cell with no smoothing (Figure S1). These spectra have been normalized by the spectra taken in the part of the electrochemical cell with no particles to account for contributions from the substrate or other scatterers in the system. Part (a) shows the spectra over the same wavelength range as that in Figure 1 of the Letter. Part (b) shows the spectra over the entire measured wavelength range. As can been seen from in the figures, there is very little noise. The signal to noise ratio was roughly 400:1.

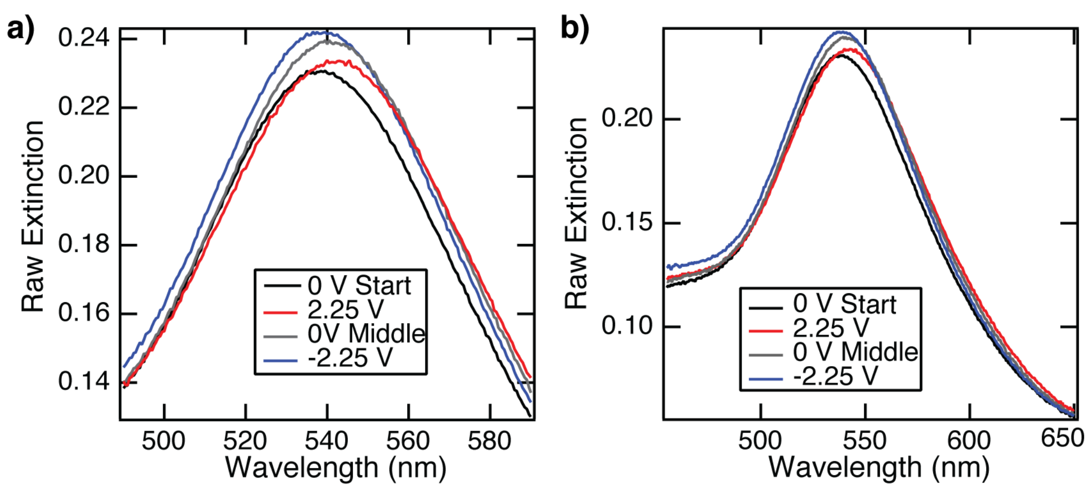

Figure S1. Normalized raw spectra at the extremes of the applied bias cycle (2.25V and -2.25V) as well as the first 0V point (0V Start) and the 0V point in the middle of the applied bias cycle (0V Middle).

Electrochemical Cell Fabrication

ITO coated glass substrates (SPI brand, 30-60 Ω, 06430) were used as the top and bottom electrodes in the electrochemical cell (Figure 1). The substrates were cleaned by ultrasonicating overnight in a solution containing equal volume of acetone, methanol, toluene, and isopropyl alcohol then dried with N_2. Parafilm wax was used to cover one half of the bottom electrode ITO slide to prevent Au colloid deposition in the subsequent step, thereby reserving half of the bottom electrode for use as a control in the normalization of optical spectra; this allowed us to carefully control for a possible optical response from the ITO substrate as a function of applied bias. The bottom electrode was placed in a glass scintillation vial (ITO-side up) with 300uL of 30nm radius Au colloids in water (BBI International, EM.GC60 Batch #16516 OD1.2) and 1.5mL of deionized (DI) water. 60 μL 0.1M HCl was added to the vial, and the vial was immediately centrifuged at 2000 rpm (~670 g-force) for 40 minutes. After centrifuging, the Au colloid solution had become clear and the bottom ITO electrode has a noticeable red color due to Au nanoparticles deposited on the surface. The Parafilm wax was removed from the bottom electrode and the electrode was rinsed thoroughly with DI water then soaked in toluene for one hour to remove residue from the Parafilm wax. Both electrodes were plasma etched with a direct plasma at 110W and 300mTorr O_2 for 20 minutes to remove ligands and any organic mater from the AuNPs and ITO surface. Substrates were then vacuum annealed at 350C for 20 minutes. The two electrodes were mounted face-to-face with two pieces of Teflon tape used as a spacer between the slides. Under inert atmosphere, DEME electrolyte (Sigma Aldrich, 727679) was used to fill the space between the slides and the cell edges were sealed with 5-minute-setting epoxy to prevent water moisture and oxygen from entering the cell.

Optical Measurement Procedures

The beam from a supercontinuum pulsed laser (20 MHz, Fianium SC400-2) was chopped at 100 Hz and directed into a monochromator (Oriel 777000) that was optically in-series with two Si photodiodes (the first photodiode was used as a reference). The spectral resolution of the monochromator was approximately 1.5 nm. The photodiode signals were passed through transimpedance amplifiers (DL Instruments 564) and were detected by lock-in amplifiers (SR830 DSP). Spectra with the optical beam passing through the portions of the bottom electrode with and without Au colloids were collected at each applied bias step. The spectra taken in the portion of the bottom electrode without Au colloids were used as normalization spectra.

Simulation Methods

As discussed in the manuscript, parameter sweeps were preformed where, for each unique parameter set (surrounding-index, Γ_V, n(V), and shell-thickness), a full-wave electromagnetic simulation was preformed with Lumerical FDTD Solutions software. We began with broad parameter sweeps with the limits shown in the Table S1. After simulations were run for all possible combinations of parameters in the broad parameter sweep, the 5 parameter sets which resulted in extinction spectra with the smallest RMSE when compared to the Savitzky-Golay experimental extinction spectra were selected. Five new parameter sweeps (one for each of the five selected parameter sets), with the selected parameters in the center of the new parameter limits and finer parameter steps (higher resolution sweep) were preformed. The five parameter sets producing the lowest RMSE fits to experiment over the five parameter sweeps were then selected. This iterative processes was preformed until an acceptable resolution (shown in the Table S1) was reached for all parameters and at this point, the parameter set with the smallest RMSE overall was selected as the champion set. This process was carried out for each applied bias and thus resulted in one champion set of parameters for each applied bias. These parameters are those shown in the Letter's Figure 5.

Table S1

Parameter	Lower Limit	Upper Limit	Finest Resolution
Surrounding Index	1.0	1.7	0.001
Shell Charge (n/n_{AU}%)	0.95	1.05	0.005
Shell Thickness (nm)	0	5	0.25
Damping (rad/s)	0	3e14	2.5e11

Comparison of Simulation and Experiment Over Full Wavelength Range

Figure S2 shows the best-fit simulation and experimental spectra for the same voltage points shown in Figure 3d in the Letter (the 0V curves are for the first 0V applied bias point at the start of the voltage cycle). It is clear from part (a) of Figure S2 that the simulations do not reproduce the broadness of the experimental spectra. We attribute the amplified broadening of the experimental spectra to non-idealities present in the experimental system that were not captured in the simulations. These non-idealities include roughness of the ITO substrate, particle-particle interactions,

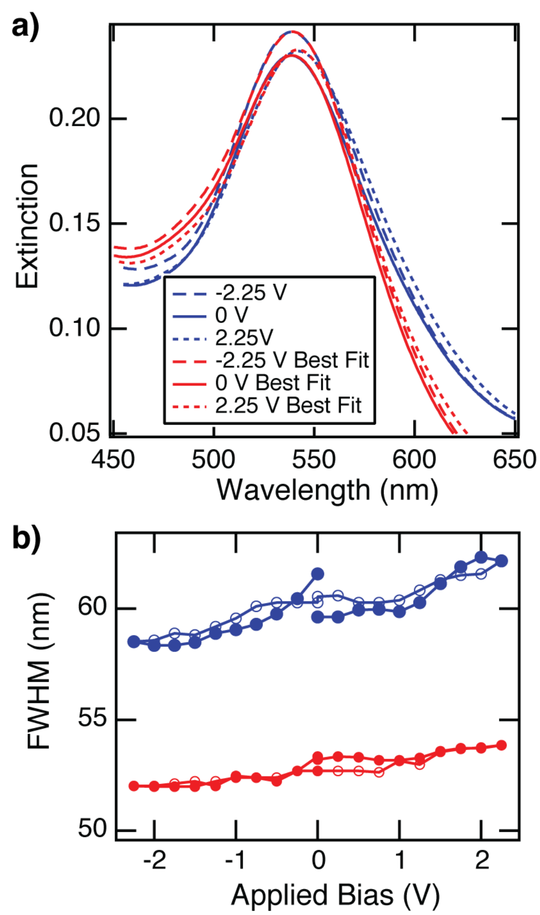

Figure S2. (a) Experimental extinction spectra at 0V, +2.25V and -2.25V and their best fit simulated spectra. (b) Absolute full width half max for experimental (blue) and simulated (red) spectra. The markers for the applied bias points for the middle portion of the cycle, from 2V to -2.25V in -0.25V steps are hollow.

and heterogeneity of the particles beyond small changes in radius that are accounted for by the simulations. Part (b) of Figure S2 shows the absolute full width at half max for the experimental spectra and the best-fit simulated spectra. The changes in this parameter, relative to the first 0V applied bias point are shown in Figure 3c in the Letter. There we show that the general trends of the changes in experimental peak broadness as a function of voltage are reproduced relatively well by the best-fit simulation peak broadness changes. However, due to the non-idealities discussed above, the full width at half max is offset between the experimental and simulated spectra by approximately 6nm throughout the applied bias cycle.

ITO Optical Data

The optical constants used to define the ITO in the FDTD simulations are given in Table S2.

Table S2:

λ(nm)	n	k	λ(nm)	n	k
400	1.99756	0.04331	418	1.97578	0.04054
401	1.99629	0.04314	419	1.97464	0.04041
402	1.99502	0.04297	420	1.9735	0.04028
403	1.99377	0.0428	421	1.97236	0.04014
404	1.99252	0.04263	422	1.97123	0.04002
405	1.99128	0.04247	423	1.97011	0.03989
406	1.99004	0.04231	424	1.96899	0.03976
407	1.98882	0.04215	425	1.96788	0.03964
408	1.9876	0.04199	426	1.96677	0.03952
409	1.98639	0.04184	427	1.96567	0.0394
410	1.98518	0.04168	428	1.96457	0.03928
411	1.98398	0.04153	429	1.96348	0.03916
412	1.98279	0.04139	430	1.96239	0.03905
413	1.98161	0.04124	431	1.96131	0.03893
414	1.98043	0.0411	432	1.96024	0.03882
415	1.97926	0.04096	433	1.95916	0.03871
416	1.97809	0.04082	434	1.9581	0.0386
417	1.97693	0.04068	435	1.95703	0.0385
			436	1.95598	0.03839

437	1.95492	0.03828	493	1.90109	0.03422
438	1.95387	0.03818	494	1.90020	0.03418
439	1.95283	0.03808	495	1.89930	0.03413
440	1.95179	0.03798	496	1.89841	0.03409
441	1.95075	0.03788	497	1.89752	0.03404
442	1.94972	0.03778	498	1.89663	0.03400
443	1.94869	0.03769	499	1.89574	0.03395
444	1.94766	0.0375	500	1.89485	0.03391
445	1.94664	0.0375	501	1.89397	0.03387
446	1.94562	0.0374	502	1.89309	0.03383
447	1.94461	0.03731	503	1.8922	0.03379
448	1.9436	0.03722	504	1.89132	0.03375
449	1.9426	0.03713	505	1.89044	0.03371
450	1.94159	0.03705	506	1.88956	0.03367
451	1.94059	0.03696	507	1.88869	0.03363
452	1.9396	0.03687	508	1.88781	0.03359
453	1.93861	0.03679	509	1.88693	0.03356
454	1.93762	0.03671	510	1.88606	0.03352
455	1.93663	0.03662	511	1.88519	0.03348
456	1.93565	0.03654	512	1.88431	0.03345
457	1.93467	0.03646	513	1.88344	0.03341
458	1.93369	0.03638	514	1.88257	0.03338
459	1.93272	0.03631	515	1.88171	0.03335
460	1.93175	0.03623	516	1.88084	0.03331
461	1.93078	0.03616	517	1.87997	0.03328
462	1.92982	0.03608	518	1.8791	0.03325
463	1.92885	0.03601	519	1.87824	0.03322
464	1.92789	0.03593	520	1.87738	0.03319
465	1.92694	0.03586	521	1.87651	0.03316
466	1.92598	0.03579	522	1.87565	0.03313
467	1.92503	0.03572	523	1.87479	0.0331
468	1.92409	0.03565	524	1.87393	0.03308
469	1.92314	0.03559	525	1.87307	0.03305
470	1.92220	0.03552	526	1.87221	0.03302
471	1.92125	0.03545	527	1.87135	0.03299
472	1.92032	0.03539	528	1.87049	0.03297
473	1.91938	0.03533	529	1.86963	0.03294
474	1.91845	0.03526	530	1.86878	0.03292
475	1.91751	0.03520	531	1.86792	0.03289
476	1.91659	0.03514	532	1.86707	0.03287
477	1.91566	0.03508	533	1.86621	0.03285
478	1.91473	0.03502	534	1.86536	0.03283
479	1.91381	0.03496	535	1.8645	0.0328
480	1.91289	0.03490	536	1.86365	0.03278
481	1.91197	0.03485	537	1.8628	0.03276
482	1.91105	0.03479	538	1.86195	0.03274
483	1.91014	0.03473	539	1.8611	0.03272
484	1.90923	0.03468	540	1.86025	0.0327
485	1.90832	0.03463	541	1.8594	0.03268
486	1.90741	0.03457	542	1.85855	0.03266
487	1.90650	0.03452	543	1.8577	0.03265
488	1.90559	0.03447	544	1.85685	0.03263
489	1.90469	0.03442	545	1.856	0.03261
490	1.90379	0.03437	546	1.85515	0.03259
491	1.90289	0.03432	547	1.8543	0.03258
492	1.90199	0.03427	548	1.85345	0.03256

549	1.85261	0.03255	600	1.8095	0.03234
550	1.85176	0.03253	601	1.80865	0.03235
551	1.85091	0.03252	602	1.8078	0.03235
552	1.85007	0.0325	603	1.80695	0.03236
553	1.84922	0.03249	604	1.8061	0.03237
554	1.84838	0.03248	605	1.80525	0.03237
555	1.84753	0.03247	606	1.8044	0.03238
556	1.84668	0.03245	607	1.80355	0.03239
557	1.84584	0.03244	608	1.8027	0.0324
558	1.84499	0.03243	609	1.80184	0.03241
559	1.84415	0.03242	610	1.80099	0.03242
560	1.84331	0.03241	611	1.80014	0.03243
561	1.84246	0.0324	612	1.79928	0.03244
562	1.84162	0.03239	613	1.79843	0.03245
563	1.84077	0.03238	614	1.79758	0.03246
564	1.83993	0.03237	615	1.79672	0.03247
565	1.83908	0.03237	616	1.79587	0.03248
566	1.83824	0.03236	617	1.79501	0.03249
567	1.8374	0.03235	618	1.79415	0.0325
568	1.83655	0.03234	619	1.7933	0.03252
569	1.83571	0.03234	620	1.79244	0.03253
570	1.83486	0.03233	621	1.79158	0.03254
571	1.83402	0.03233	622	1.79072	0.03256
572	1.83318	0.03232	623	1.78987	0.03257
573	1.83233	0.03232	624	1.78901	0.03258
574	1.83149	0.03231	625	1.78815	0.0326
575	1.83064	0.03231	626	1.78729	0.03261
576	1.8298	0.0323	627	1.78642	0.03263
577	1.82896	0.0323	628	1.78556	0.03265
578	1.82811	0.0323	629	1.7847	0.03266
579	1.82727	0.0323	630	1.78384	0.03268
580	1.82642	0.03229	631	1.78297	0.03269
581	1.82558	0.03229	632	1.78211	0.03271
582	1.82474	0.03229	633	1.78125	0.03273
583	1.82389	0.03229	634	1.78038	0.03275
584	1.82305	0.03229	635	1.77952	0.03276
585	1.8222	0.03229	636	1.77865	0.03278
586	1.82136	0.03229	637	1.77778	0.0328
587	1.82051	0.03229	638	1.77691	0.03282
588	1.81966	0.03229	639	1.77605	0.03284
589	1.81882	0.0323	640	1.77518	0.03286
590	1.81797	0.0323	641	1.77431	0.03288
591	1.81713	0.0323	642	1.77344	0.0329
592	1.81628	0.0323	643	1.77256	0.03292
593	1.81543	0.03231	644	1.77169	0.03294
594	1.81459	0.03231	645	1.77082	0.03296
595	1.81374	0.03231	646	1.76995	0.03298
596	1.81289	0.03232	647	1.76907	0.03301
597	1.81204	0.03232	648	1.7682	0.03303
598	1.8112	0.03233	649	1.76732	0.03305
599	1.81035	0.03233	650	1.76645	0.03307